

REMARKS

Reconsideration and withdrawal of the rejections made in the mentioned Office Action are respectfully requested, in view of the foregoing amendments and the following remarks.

Summary of Amendments

By the foregoing amendments claims 1-30 are canceled and new claims 31 to 60 are added, whereby claims 31-60 are pending in the present application. Claims 31, 45 and 59 are independent claims. Support for the added claims can be found throughout the present specification and, in particular, in canceled claims 1-30.

It is noted that the cancellation of claims 1-30 is without prejudice or disclaimer, and Applicants expressly reserve the right to prosecute these claims in one or more divisional and/or continuation applications.

Response to Interview Summary

The Examiner's summary of the telephonic interview of December 3, 2003 correctly sets forth the substance of the interview.

Summary of Office Action

As an initial matter, Applicants note with appreciation that the claim for foreign priority under 35 U.S.C. § 119(a)-(d) and receipt of the certified copies of the priority

P21645.A05

documents have been acknowledged in the present Office Action and that an initialed and signed copy of the Form PTO-1449 which was submitted in the Information Disclosure Statement filed February 28, 2002 has been returned together with the Office Action mailed October 6, 2003.

Claim 5 is rejected under 35 U.S.C. § 112, second paragraph, as allegedly being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as his invention.

Claims 1, 4-14 and 16-27 are rejected under 35 U.S.C. § 102(e) as allegedly being anticipated by U.S. Patent No. 6,598,645 to Larson (hereafter "LARSON I").

Claims 1 and 5-29 are rejected under 35 U.S.C. § 102(e) as allegedly being anticipated by Published Patent Application US 2003/032710 A1 by Larson (hereafter "LARSON II").

Claims 1-3, 16, 17, 19, 21, 23 and 24 are rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by U.S. Patent No. 5,576,372 to Kresge et al. (hereafter "KRESGE").

Claims 4-15 are rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over KRESGE in view of U.S. Patent No. 6,034,164 to Elspass et al. (hereafter "ELSPASS").

Claims 28-30 are rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over LARSON I in view of U.S. Patent No. 5,250,630 to Oshima et al. (hereafter "OSHIMA").

P21645.A05

Claims 28-30 are rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over LARSON II in view of OSHIMA.

Response to Office Action

Reconsideration and withdrawal of the rejections of record are respectfully requested.

Response to Rejection under 35 U.S.C. § 112, Second Paragraph

Claim 5 is rejected under 35 U.S.C. § 112, second paragraph, as allegedly being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as his invention. In this regard, the Examiner takes the position that the recitation of the term "substituted" in connection with the meanings of the radicals R of the ammonium cation renders claim 5 indefinite since it is allegedly not clear what exactly are the substituents on the R group.

This rejection is respectfully traversed. It is readily apparent to one of ordinary skill in the art which substituents on the alkyl, aryl and benzyl groups recited in claims 36 and 50 (which are derived from claim 5) are suitable and desirable, respectively for the claimed purpose, i.e., in ammonium ions which are used to modify a layered silicate in a rubber compound for a tire tread rubber. It is noted that the Examiner has not cited any documents which would support the allegation that one of ordinary skill in the art would not know what the substituents on the radicals R are. Further, the Examiner is respectfully reminded that

P21645.A05

longstanding case law expressly makes clear that "unsubstituted or substituted" is not considered indefinite and thus is clear under 35 U.S.C. § 112 ¶2. *Bosies v. Benedikt*, 30 USPQ2d 1862, 1863 (Fed. Cir. 1994) (claims included "het is a substituted or unsubstituted heterocyclic...") and *In re Baird*, 29 USPQ2d 1550, 1551 (Fed. Cir. 1994) (claims included "R is selected from substituted and unsubstituted alkylene radicals..."). Accordingly, this rejection should be withdrawn, which action is respectfully requested.

Response to Rejection of Claims under 35 U.S.C. § 102(e) over LARSON I

Claims 1, 4-14 and 16-27 are rejected under 35 U.S.C. § 102(e) as allegedly being anticipated by LARSON I. The rejection alleges that LARSON discloses a composition for a tire comprising a usual reinforcing filler such as carbon black and intercalated clay. The rejection further alleges that the composition of LARSON is utilized in tire components such as sidewall inserts and optionally apex. The Examiner also asserts that the clay used in LARSON, i.e., CLOSITE 25A, allegedly "consists of montmorillonite clay intercalated with dimethyl hydrogenated ditallow ammonium chloride, wherein tallow is aliphatic hydrocarbon having 16-18 carbon atoms". The rejection also contends that further features recited in the rejected claims are disclosed in LARSON I.

Applicants respectfully submit that the rejection of the claims as allegedly anticipated by LARSON I is moot in view of claims 31-60 submitted herewith. In particular,

P21645.A05

independent claim 31 is directed to a tire tread which comprises the sulfur-curable rubber compound recited in canceled claim 1. LARSON I does not teach or suggest the use of the rubber compound disclosed therein for making a tire tread. Accordingly, LARSON does not anticipate the subject matter of claim 31 for this reason alone.

Independent claim 45 corresponds generally to a combination of canceled claims 1, 2 (in part) and 22. Claim 2 has not been rejected as anticipated by LARSON I (apparently because LARSON I does not disclose a rubber compound comprising about 40 phr or more of modified layered silicate), wherefore the same reasoning in support of patentability should apply to claim 45.

Independent claim 59 corresponds generally to canceled claim 28. The latter claim has not been rejected as anticipated by LARSON I, wherefore the same reasoning in support of patentability applies to claim 59.

Additionally, Applicants respectfully submit that they could not find any information regarding the composition of CLOSITE 25A as asserted by the Examiner in LARSON I (and LARSON II). Accordingly, should the Examiner maintain the rejection over LARSON I, the Examiner is respectfully requested to provide written evidence regarding the alleged composition of CLOSITE 25A to provide Applicants with a full and fair opportunity to address this rejection in its entirety.

For at least the reasons set forth above, the rejection of the claims under 35 U.S.C. §

P21645.A05

102(e) over LARSON I is moot, and withdrawal thereof is respectfully requested.

Response to Rejection of Claims under 35 U.S.C. § 102(e) over LARSON II

Claims 1 and 5-29 are rejected under 35 U.S.C. § 102(e) as allegedly being anticipated by LARSON II.

In this regard, it is submitted that the present application claims priority under 35 U.S.C. § 119 of German Patent Application No. 100 59 236.8 filed November 29, 2000. LARSON II, on the other hand, was filed on July 2, 2001, i.e., more than seven months after the priority date of the present application.

Submitted herewith is a verified English language translation of German Patent Application No. 100 59 236.8. Since all of present claims 31-60 are believed to be supported by the priority document, LARSON II does not qualify as prior art under 35 U.S.C. § 102(e) for present claims 31-60, wherefore the rejection under 35 U.S.C. § 102(e) over LARSON II is moot and should be withdrawn, which action is respectfully requested.

Response to Rejection of Claims under 35 U.S.C. § 102(b) over KRESGE

Claims 1-3, 16, 17, 19, 21, 23 and 24 are rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by KRESGE. The rejection alleges that KRESGE discloses a composition for tire inner liners comprising clay intercalated with reactive rubber, wherein the reactive rubber allegedly contains ammonium cations. The Office Action asserts that the

P21645.A05

content of the layered silicate of KRESGE is in the range of 1-50 phr and that other elements which are recited in the rejected claims are disclosed in KRESGE as well.

Applicants respectfully submit that this rejection of the claims under 35 U.S.C. § 102(b) as allegedly anticipated by KRESGE is moot in view of claims 31-60 submitted herewith. In particular, independent claim 31 is directed to a tire tread which comprises the sulfur-curable rubber compound recited in canceled claim 1. KRESGE does not teach or suggest the use of the rubber compound disclosed therein for making a tire tread. For this reason alone, KRESGE does not anticipate the subject matter of claim 31.

Independent claim 45 corresponds generally to a combination of canceled claims 1, 2 (in part) and 22. Claim 22 has not been rejected as anticipated by KRESGE, wherefore the same reasoning in support of patentability should apply to claim 45.

Independent claim 59 corresponds generally to canceled claim 28. Claim 28 has not been rejected as anticipated by KRESGE, wherefore the same reasoning in support of patentability should apply to claim 59.

For at least the reasons set forth above, the rejection of the claims under 35 U.S.C. § 102(b) over KRESGE is moot, and withdrawal thereof is respectfully requested.

***Response to Rejection of Claims under 35 U.S.C. 103(a) over KRESGE in view of
ELSPASS***

Claims 4-15 are rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over KRESGE in view of U.S. Patent No. 6,034,164 to Elspass et al. (hereafter "ELSPASS").

P21645.A05

In this regard, the rejection asserts that the difference between KRESGE and the present invention is the use of an ammonium compound instead of a functionalized rubber and that ELSPASS allegedly discloses a composition for a tire inner liner comprising exfoliated clay, with the clay being intercalated with a dialkylammonium salt before it is incorporated into the rubber composition. The Examiner takes the position that in light of this asserted disclosure it would allegedly have been obvious to one having ordinary skill in the art to utilize the ammonium compounds of ELSPASS in the composition of KRESGE and thereby obtain the claimed invention.

Applicants respectfully submit that this rejection is moot in view of claims 31-60 submitted herewith. In particular, both ELSPASS and KRESGE relate to rubber compounds for tire inner liners, as acknowledged by the Examiner. In contrast, present independent claim 31 is directed to a tire tread. As one having ordinary skill in the art is aware, the requirements which a tire inner liner on the one hand and a tire tread on the other hand have to satisfy are very different. For example, one of the main requirements for tire inner liners is that they are gas-impervious. Tire treads are required to provide, *inter alia*, a good traction and grip. Accordingly, one of ordinary skill in the art would not be motivated to consider the teachings of KRESGE/ELSPASS for the production of a tire tread. For this reason alone, the subject matter of claim 31 and the claims dependent therefrom is not rendered obvious by a combination of KRESGE and ELSPASS.

P21645.A05

Independent claim 45 corresponds generally to a combination of canceled claims 1, 2 (in part) and 22. Claim 22 has not been rejected as unpatentable over KRESGE in view of ELSPASS, wherefore the same reasoning in support of patentability should apply to claim 45.

Independent claim 59 corresponds generally to canceled claim 28. Claim 28 has not been rejected as unpatentable over KRESGE in view of ELSPASS, wherefore the same reasoning in support of patentability should apply to claim 59.

For at least the reasons set forth above, the rejection of the claims under 35 U.S.C. § 103(a) over KRESGE in view of ELSPASS is moot, and withdrawal thereof is warranted and respectfully requested.

Response to Rejection of Claims under 35 U.S.C. 103(a) over LARSON I in view of OSHIMA

Claims 28-30 are rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over LARSON I in view of OSHIMA.

In this regard, the rejection alleges that the difference between the present invention and the disclosure of LARSON I is making of a tire tread and its use in a racing tire. The rejection further asserts that OSHIMA discloses a rubber composition for a pneumatic tire and that fillers utilized in the tire tread of the composition of OSHIMA include clay as adequate for use. The rejection further contends that the rubber composition of OSHIMA is utilized in a racing tire since it provides good grip at high temperatures. In view of this

P21645.A05

alleged disclosure the Examiner takes the position that it would allegedly “have been obvious to one having ordinary skill in the art to utilize the composition of LARSON I in the tire tread or in the racing tire, since the composition would also exhibit the good grip”.

This rejection is respectfully traversed. The only similarity between the teachings of LARSON I and OSHIMA that the Examiner appears to have identified is that both documents relate to rubber compounds which are useful in the manufacture of tires and which may comprise clay as a filler. However, there is no motivation for one having ordinary skill in the art to combine the teachings of LARSON I and OSHIMA for merely this reason.

For example, LARSON I does not even relate to tire treads, let alone teach or suggest that tire treads made from the compositions disclosed therein would exhibit good grip. The Examiner has apparently arrived at this conclusion by applying hindsight, i.e., after having read the present application.

Also, according to OSHIMA (non-intercalated) clay is not a mandatory and not even a particularly desirable component of the compositions disclosed therein. In particular, in the passage from col. 3, line 60 to col. 4, line 4, OSHIMA merely states that the reinforcement to be incorporated into the rubber composition is not specifically limited to a certain kind, but that carbon blacks having an average diameter of 10-500 nm are preferably employed, whereas alternatively, calcium carbonate, clay, talc and the like may be “adequately employed” as a filler. This very general disclosure is a disincentive rather than an incentive

P21645.A05

to use clay as a filler in the tire tread compositions of OSHIMA. It certainly does not provide any motivation to use the particular clay disclosed in LARSON I, which document does not even relate to tire treads.

Applicants submit that at least for the reasons discussed above, the rejection of claims 28-30 (which are similar to present claims 43, 44 and 59) under 35 U.S.C. § 103(a) as obvious over LARSON I in view of OSHIMA is not tenable, wherefore withdrawal of this rejection is warranted and respectfully requested.

Response to Rejection of Claims under 35 U.S.C. 103(a) over LARSON II in view of OSHIMA

Claims 28-30 are rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over LARSON II in view of OSHIMA.

As already set forth above with regard to the rejection of the claims under 35 U.S.C. § 102(e), in view of the submission of a verified English language translation of the priority document of the present application, LARSON II does not qualify as prior art, wherefore the rejection of the claims over LARSON II in view of OSHIMA is moot and withdrawal thereof is warranted and respectfully requested.


CONCLUSION

In view of the foregoing, it is believed that all of the claims in this application are in condition for allowance, which action is respectfully requested. If any issues yet remain

P21645.A05

which can be resolved by a telephone conference, the Examiner is respectfully invited to telephone the undersigned at the telephone number below.

Respectfully submitted,
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VERIFICATION OF TRANSLATION

I, Heribert Muensterer

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declare that I am well acquainted with both the German and English languages, and that the attached is an accurate translation, to the best of my knowledge and ability, of the German language Patent Application No. 100 59 236.8, filed November 29, 2000.

I further declare that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and, further, that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the above-captioned application or any trademark issued thereon.

Signature Heribert Muensterer
Heribert Muensterer

Date 2/24/04

Rubber Mixture for Tire Treads

The invention relates to a sulfur-curable rubber mixture for tire treads, in particular for tire treads of racing tires, that contain at least one diene rubber, at least one filler, plasticizer, and further usual additives. Furthermore, it relates to vehicle tires, in particular, racing tires the tread of which contains this rubber mixture.

Various fillers, such as carbon black, silica, aluminosilicates, china clay, metal oxides, or chalk, for example, are added to rubber mixtures for tire treads. Due to their specific effect on the rubber the fillers not only help to lower the cost of the rubber mixtures but also influence the characteristics of the uncured rubber mixture and the tires made therefrom. Active fillers, also called reinforcing fillers, including the majority of carbon blacks, silica, and the majority of finely divided silicates, generally improve a number of characteristics of the vulcanized material, such as strength, tension value (module), and tear strength, while other characteristics such as elongation at break and rebound resilience are influenced negatively. Here, the activity of the filler depends on the particle size, the specific surface area, the geometric shape of the surface, and the chemical composition.

In the past, the known fillers were studied, altered, and modified in multiple ways in order to optimize the characteristics of tires containing these fillers. Additionally, new classes of fillers were developed in this context.

One of these classes of fillers is sheet silicates; sheet silicates resulting in the problem that sheet silicates are not compatible with conventional rubbers due to their polar surface, i.e., they must be modified prior to incorporating them into a rubber mixture such that they are organophilic and compatible with the surrounding rubber matrix. This is the only way the sheet silicate can be well distributed in the rubber matrix. In order to achieve this, it has been known for a long time to modify the normally hydrophilic surface of the sheet silicates

by a cation exchange with alkylammonium ions such that they become organophilic. Then the individual organically modified layers are stacked parallel and form small stacks in which organic and inorganic layers alternate regularly.

5 An overview of nanocomposites based on polymers and sheet silicates, their production, characterization, and use can be found, e.g., in the article "Polymer layered silicate nanocomposites" by M. Zanetti, S. Lomakin, and G. Camino in *Macromol, Mater. Eng.* 279, p. 1 - 9, (2000.)

10 Four methods for producing nanocomposites based on polymers and sheet silicates are presented therein: in-situ polymerization, intercalation of the polymer from a solution, direct intercalation of molten polymer, and sol/gel technology. These processes cause the individual layers of the silicate to be expanded and sometimes even be completely unfoiled (exfoliated). The individual layers have a thickness of approximately 1 nm and are
15 surrounded by polymer. The presence of nanocomposites in polymer materials renders it possible to endow the polymer products made therefrom with new and improved characteristics. The concept of nanocomposites based on sheet silicates is used primarily in the area of thermoplastics, in order to improve their characteristics, for example, with respect to tensile strength. The four above-mentioned processes for producing nanocomposites can
20 be used for thermoplastics, while for rubbers the direct intercalation of the molten polymer is impossible due to the high viscosity in the conventional temperature range for processing. The other three processes can also be used for rubber, however, these processes are technologically very expensive and always involve the use of solvents, which in general have to be removed entirely in the further course of the processing of such nanocomposites, e.g.,
25 for the incorporation into a curable rubber mixture.

From WO 97/00910 it is known to produce a latex which contains sheet silicate having intercalated emulsion polymer. For the production of such a latex, initially the sheet

silicate is rendered organophilic by an ion exchange with onium salts and, subsequently, in an emulsion a rubber is polymerized from its monomers in the presence of the organophilic sheet silicate into the layers of the silicate. Thus nanocomposites are formed. After the coagulation and drying, such nanocomposites can be used in rubber mixtures, e.g., for rubbers of tire inner liners with a reduced gas permeability.

US 5,576,372 describes the use of sheet silicates in the rubber of tire inner liners with a reduced gas permeability, with the sheet silicates being provided with a reactive rubber having positively charged groups. Here, the sheet silicates are treated with a solution containing the reactive rubber, generally a solution having an organic solvent such as toluene. The reactive rubber swells into and between the layers. Subsequently, all solvents must be removed prior to further processing, e.g., the incorporation into the rubber mixture of the tire inner liner. Additionally, many organic solvents must be considered ecologically and toxicologically questionable.

Specially treated sheet silicates for rubber mixtures with improved mechanical characteristics and reduced gas permeability are known from US 6,103,817 as well. Prior to the incorporation into the rubber mixture, the special sheet silicates are rendered organophilic by an ion exchange with onium salts and, subsequently, additional organic guest molecules are introduced/swelled in from an organic solvent or by treating the organophilic sheet silicates with the liquid guest molecules (in substances having a low melting point), in order to increase the distance between the layers in the sheet silicate and to facilitate and improve the distribution in the rubber mixture. One or two different substances may be introduced into the sheet silicate, and at least one substance must have polar groups.

The three processes described have in common that prior to the mixing into a rubber mixture, the sheet silicates are made by expensive processes such that prior to incorporation the separate silicate layers are already separated from one another by rubber molecules so that nanocomposites are present.

From US 6,034,164 it is known to incorporate sheet silicates modified with alkyl-ammonium ions directly into a rubber mixture of two special rubber compounds without any prior swelling or polymerization thereinto of rubber or guest molecules. The rubber compounds in question are, on the one hand, a non-ionic polymer having a molecular weight > 50000 g/mol and, on the other hand, a non-ionic polymer compatible with the first polymer and with a molecular weight lower than that of the first polymer. The forces acting during the mixing process result in layer packages of modified sheet silicate having a thickness of more than 10 nm. This is to avoid complete exfoliation. Such rubber mixtures may be used for the production of gas impermeable elastomer membranes, such as rubber of tire inner liners or bladders.

Rubber mixtures used for rubbers of tire inner liners (main purpose: gas impermeability) are generally insufficient to meet the requirements of rubber mixtures of tire treads. For example, the rubber mixtures used for tire treads must cause the tires to be optimized with respect to wear, skidding performance, roll resistance, heat build up, tear propagation resistance, and cold flexibility. Treads of racing tires for, e.g., race cars or race karts primarily requires a high skidding resistance and a good grip at temperatures present during operation. Such high skidding resistance can take place by increasing the dissipation factor $\tan \delta$ in the relevant temperature range, e.g., by incorporating large amounts (> 100 phr) of high energy dissipating carbon blacks, so-called racing carbon blacks. Furthermore, it is advantageous for the tires to have a Shore hardness as low as possible in the temperature range during operation.

Thus, the present invention is based on the object to provide a rubber mixture for tire treads, in particular, for tire treads of racing tires, that can be produced easily and more environmentally friendly and that results in a high skidding resistance (high friction coefficient, good grip) in the tires made therefrom combined with a reduction in hardness at elevated temperatures.

5 This object is attained according to the invention in that, relative to 100 parts by weight of the overall rubber components in the rubber mixture, the rubber mixture features 5 to 90 phr of at least one sheet silicate that is modified with alkylammonium ions having the general formula $^+NR_4$, and is free of any additional guest molecules swelled or polymerized into it by prior treatment.

10 The unit phr (parts per hundred parts of rubber by weight) used in this document is the usual measurement unit for quantities for mixture formulations in the rubber industry. The dosage of parts by weight of the individual substances is here always given with respect to 100 parts by weight of the overall mass of all rubbers present in the mixture.

15 Surprisingly, due to the incorporation of the sheet silicate modified with alkylammonium ions which has no additional guest molecules incorporated by a prior treatment, into rubber mixtures for tread rubbers it can be achieved that, compared to conventional mixtures of carbon black, the vulcanized materials show a distinct increase of the friction coefficient and, thus, in skidding resistance at temperatures above 0°C and, particularly, at temperatures of approximately 40 to 70°C which are present in the treads during operation. This effect can be achieved with the amounts of sheet silicate mentioned. Unlike with racing carbon blacks, it is not necessary to increase the amount of fillers in the mixture to high filling levels of more than 100 phr, which levels are associated with disadvantages in other tire characteristics, such as abrasion and tear resistance.

20 According to an advantageous embodiment of the invention, the rubber mixture features 40 to 95 phr of the sheet silicate. The best results can be achieved with respect to an increase of the skidding resistance with these dosages.

All natural and synthetic sheet silicates known to one of skill in the art and suitable for ion exchange, such as montmorillonites, smectites, china clays, and their mixtures, e.g.,

that occur naturally in the form of various clay minerals (e.g., bentonite and china clay), can be used as the starting material for the modified sheet silicates. The individual layers of the sheet silicates used should have a thickness of 0.8 to 2.0 nm and a mean diameter of 80 to 800 nm. The small, extremely thin lamellae can be optimally dispersed in the rubber mixture and bonded thereto.

The surface of the sheet silicates is modified by a cation exchange with alkylammonium ions having the general formula $^+NR_4$, the modified sheet silicate having a preferred carbon content of 5 to 50 percent by weight. The R used in the alkylammonium ion for the modification can be different or identical and selected from the group consisting of hydrogen, substituted or unsubstituted, saturated or unsaturated alkyl groups having 1 to 40 carbon atoms with or without branching and substituted or unsubstituted aryl and benzyl groups with at least one R being a substituted or unsubstituted, saturated or unsaturated alkyl group with more than 8 carbon atoms. In this way, sheet silicates are created with the distance between the separate layers being 1.1 to 5 nm prior to an additional processing or incorporation. It is particularly preferred when the sheet silicate used for the rubber mixture according to the invention is modified with a dimethyl dioctadecylammonium ion. Sheet silicates modified in this way have proven particularly advantageous in increasing the skidding resistance.

The sulfur-curable rubber mixture contains at least one diene rubber. Diene rubbers are all rubbers with an unsaturated carbon chain that are derived at least partially from conjugated dienes. It is particularly preferred when the diene rubber or the diene rubbers is or are selected from the group consisting of natural rubber, synthetic polyisoprene, polybutadiene, and styrene-butadiene copolymer. These diene elastomers are easily processed into the rubber mixture according to the invention and show good characteristics of the vulcanized material.

The rubber mixture may contain polyisoprene (IR, NR) as a diene rubber. This may be either a cis-1,4-polyisoprene or a 3,4-polyisoprene. However, the use of cis-1,4 polyisoprene with a cis-1,4 content of > 90 % is preferred. On the one hand, such a polyisoprene may be obtained by a stereospecific polymerization in a solution with Ziegler-Natta-catalysts or using finely dispersed lithium alkyls. On the other hand, the natural rubber (NR) is such a cis-1,4-polyisoprene, the content of cis-1,4 in the natural rubber compound being higher than 99 %.

When using natural rubber the processing characteristics can be improved and the unvulcanized strength, building tack, notch resistance, and tear propagation resistance of the vulcanized materials are increased.

When the rubber mixture contains polybutadiene (BR) as the diene rubber, it may be either a cis-1,4 as well as a vinyl polybutadiene (40-90 % vinyl content). Preferred is the use of cis-1,4-polybutadiene having a cis-1,4 content of higher than 90 %, which may be produced, e.g, by a solvent polymerization in the presence of catalysts of the rare earths type.

The styrene-butadiene-copolymer may be a solution polymerized styrene-butadiene-copolymer (S-SBR) having a styrene content of approximately 10 to 45 percent by weight and a 1,2-content of 10 - 70 %, which may be produced, for example, by using lithium alkyls in organic solvents. However, emulsion polymerized styrene-butadiene-copolymers (E-SBR) and mixtures of E-SBR and S-SBR may be used as well. The styrene content of E-SBR is approximately 15 to 50 percent by weight and types known from the prior art may be used, which have been obtained in an aqueous emulsion by the copolymerization of styrene and 1,3-butadiene. E-SBR in mixtures can provide processing improvements compared to S-SBR.

However, in addition to the diene rubbers mentioned, the mixture may also contain

other types of rubber, such as styrene-isoprene-butadiene-terpolymer, butyl rubber, halobutyl rubber, acrylonitrile-butadiene rubber, hydrogenated acrylonitrile-butadiene rubber, epoxidized natural rubber, hydroxylated natural rubber, or ethylene-propylene-diene rubber (EPDM).

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According to an advantageous embodiment of the invention, the rubber mixture comprises 2 to 50 phr of at least one plasticizer oil, such as, e.g., skidding resistance and hardness.

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The rubber mixture according to the invention may additionally comprise 0 to 85 phr, preferably 5 to 50 phr, carbon black as further filler, with the sum of the amounts of carbon black and sheet silicate in the mixture not to exceed 90 phr. The addition of carbon black provides advantages in processing technology, and carbon black is an inexpensive filler.

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In addition to sheet silicate and carbon black, the rubber mixtures according to the invention may include additional fillers known to one of skill in the art, such as silica, alumina, aluminosilicates, chalk, starch, magnesium oxide, titanium dioxide, or rubber gels.

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Advantageously, the rubber mixture contains at least one silane coupling agent. The silane coupling agent serves to bond the sheet silicate to the surrounding rubber molecules. During the mixing of the rubber and/or the rubber mixture (in situ) the silane coupling agent reacts with the surface silanol groups of the sheet silicates that are not occupied by alkyl-ammonium ions. All silane coupling agents, known to one of skill in the art for use in rubber mixtures and also known for bonding silica to rubber, may be used as silane coupling agents.

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Such coupling agents known from the prior art are bifunctional organosilanes having at least one alkoxy, cycloalkoxy, or phenoxy group as the leaving group at the silicon atom and, which as other functionality, feature a group that, optionally after a cleavage thereof, may undergo a chemical reaction with the polymer. The latter groups can be the following

chemical groups, for example: -SCN, -SH, -NH₂, or -S_x- (with x=2-8). As silane coupling agents may thus be used, e.g., 3-mercaptopropyl triethoxysilane, 3-thiocyanato-propyl trimethoxysilane, or 3.3'-bis(triethoxysilyl propyl) polysulfide having 2 to 8 sulfur atoms, such as, e.g., 3.3'-bis(triethoxysilyl propyl) tetrasulfide (TESPT), the corresponding disulfide or a mixture of sulfides with 1 to 8 sulfur atoms having different contents of the various sulfides. TESPT may also be added, for example, as a blend with industrial carbon black (trade name X50S by Degussa). The level of coupling of the sheet silicate to the surrounding rubber molecules may be influenced by the dosed addition of various amounts of sheet silicate and, thus, the intensity of the hysteresis loss and the amplifying effect and, thus, the skidding resistance can be adjusted over a wide range.

Furthermore, the rubber mixture according to the invention may contain usual additives in usual parts by weight. These additives include, e.g., anti-aging agents, such as, e.g., N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylene-diamine-(6PPD), N-isopropyl-N'-phenyl-p-phenylenediamine-(IPPD), 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), and other substances such as the ones known from J. Schnetger, *Lexikon der Kautschuktechnik*, 2nd Edition, Hüthig Buch Verlag, Heidelberg, 1991, p. 42-48, processing aids such as, e.g., zinc oxide and fatty acids like stearic acid, waxes, and mastication agents such as, e.g., 2.2'-dibenzamido diphenyldisulfide (DBD).

The vulcanization is performed in the presence of sulfur or sulfur donors where some sulfur donors may simultaneously act as vulcanization accelerators as well. Here, as sulfur donors can be used, e.g., thiuram derivatives such as tetramethyl thiuram disulfide and dipentamethylene thiuram tetrasulfide, morpholine derivatives, such as dimorpholyl disulfide, dimorpholyltetrasulfide, and 2-morpholino-dithiobenzothiazole, as well as caprolactam-disulfide. In the last mixing step, sulfur and sulfur donors are added to the rubber mixture in the conventional amounts known to one of skill in the art (0.4 to 4 phr sulfur, preferably in amounts of 1.5 to 2.5 phr).

Furthermore, the rubber mixture may contain substances in conventional amounts which influence the vulcanization, such as vulcanization accelerators, vulcanization retarders, and vulcanization activators, in order to control the required time and/or the required temperature of the vulcanization and to improve the characteristics of the vulcanized material. Here, the vulcanization accelerators may be selected, for example, from the following groups of accelerators: thiazole accelerators such as, e.g., 2-mercapto-benzothiazole, sulfenamide accelerators such as, e.g., benzothiazyl-2-cyclohexyl sulfenamide, guanidine accelerators, such as, e.g., diphenyl guanidine, thiuram accelerators such as, e.g., tetrabenzyl thiuram disulfide, dithiocarbamate accelerators, such as, e.g., zinc dibenzyl dithiocarbamate, amine accelerators, such as, e.g., cyclohexyl ethylamine, thioureas such as, e.g., ethylene thiourea, xanthogenate accelerators, disulfides. The accelerators can be used in combination with one another, which may result in synergistic effects.

The production of the rubber mixture according to the invention takes place in a conventional manner in one or several mixing steps. Subsequently, it is further processed and shaped into the form desired. Then it is vulcanized in a manner known to one of skill in the art, with the resulting products having advantages with respect to tensile value, tear propagation resistance, and elongation at break.

The production of the rubber mixture according to the invention occurs in a conventional manner in one or more mixing steps. Subsequently, it is further processed, e.g., by an extrusion process, and shaped into the respective form of a tread blank. A tread mixture blank produced in this manner is applied in a known fashion during the production of a green cover, in particular, a vehicle pneumatic green cover. However, the tread in the form of a rubber mixture strip may also be wound onto a green cover which already comprises all tire parts except for the tread. After the vulcanization of the vehicle tire, the tire has advantages in skidding resistance, which is particularly important for racing tires. It is irrelevant for the tire, whether the entire tread is made from a single mixture or has, e.g.,

a cap and base structure, because what is important is that at least the surface that comes into contact with the road is made from the rubber mixture according to the invention.

In the following the invention is explained using some working examples that are summarized in Table 1, but without being limited to these examples.

In all exemplary mixtures contained in Table 1 the quantities given are parts per weight relative to 100 parts per weight of the entire rubber (phr). All mixtures could easily be mixed in processes known to one of skill in the art without any problems. Mixtures marked V serve as comparison mixtures; they contain carbon black. E marks mixtures according to the invention which feature a modified sheet silicate. The mixtures 1 and 2 differ in the rubber used.

The various mixtures were vulcanized to test specimens under pressure at 160 °C for optimal vulcanization times determined by means of rheometer curves. The material characteristics typical for the rubber industry were determined using these test specimens. The following test processes were used for examining the test specimens:

- tensile strength at room temperature according to DIN 53 504
- elongation at break at room temperature according to DIN 53 504
- tensile values at 100, 200, and 300 % elongation at room temperature according to DIN 53 504
- tear strength at room temperature according to DIN 53 504
- Shore-A hardness at room temperature and at 70 °C according to DIN 53 505
- rebound elasticity at room temperature and at 70 °C according to DIN 53 512
- dissipation factor $\tan \delta$ at 0, 30, and 60 °C according to DIN 53 513

Table 1

Components	Unit	V1	E1	V2	E2
natural rubber	phr	60	60	-	-
polybutadiene ¹	phr	40	40	-	-
E-SBR ²	phr	-	-	100	100
carbon black N220	phr	50	-	80	-
modified sheet silicate ³	phr	-	50	-	80
aromatic oil	phr	5	5	40	40
stearic acid	phr	2	2	2	2
zinc oxide	phr	3	3	3	3
anti-aging agents	phr	1	1	1	1
sulfur	phr	2	2	2	2
accelerators	phr	2.5	2.5	2.5	2.5
Characteristics					
tensile strength	MPa	20.0	9.2	15.2	3.6
elongation at break	%	406	497	523	559
tensile value 100%	MPa	2.96	2.52	1.35	1.11
tensile value 200%	MPa	8.18	3.73	3.35	1.72
tensile value 300%	MPa	15.04	5.35	6.83	2.35
tear strength	N	31.7	21.1	27.8	10.7
Shore hardness at RT	Shore A	67.5	66.6	53.3	42.7
Shore hardness at 70°C	Shore A	65.7	47.0	51.2	27.9
rebound elasticity at RT	%	58.1	43.7	47.0	17.0
rebound elasticity at 70°C	%	64.5	38.1	60.6	29.2
Dissipation factor tan δ at 0°C	-	0.109	0.160	0.278	0.393

Dissipation factor $\tan \delta$ at 30°C	-	0.065	0.248	0.237	0.433
Dissipation factor $\tan \delta$ at 60°C	-	0.061	0.210	0.194	0.334

¹ Ubepol 150, Ube Industries, Japan

² Type SBR 1500

³ sheet silicate montmorillonite modified with dimethyl dioctadecylammonium ions, carbon content approximately 30 percent by weight

As discernible from Table 1, the hardness of the vulcanized materials from the mixtures according to the invention having the sheet silicate is lower than that of the respective vulcanized materials from mixtures having carbon black, particularly at elevated temperature. Additionally, the mixtures according to the invention show a distinct increase in the dissipation factors of the vulcanized materials at 0, 30, and 60 °C compared to the mixtures containing only carbon black as a filler. A high dissipation factor correlates with a high friction coefficient and this, in turn, is a gauge for the skidding resistance and/or the grip of the tire on the road. The mixtures according to the invention are also particularly suitable for tires requiring a high grip, such as, e.g., racing tires.

The dissipation factors determined for the mixtures E1 and E2 are within an order of magnitude which is also found in conventional race car tires, which have base mixtures having contents of more than 100 phr of high energy-dissipating carbon blacks. A typical carbon black racing mixture shows, e.g., the following dissipation factors: $\tan \delta$ (0 °C) = 0.53; $\tan \delta$ (30 °C) = 0.38; $\tan \delta$ (60 °C) = 0.30. At 30 and 60 °C, the dissipation factors of the mixture E2 are even above these values.

Claims

1. Sulfur-curable rubber mixture for tire treads, in particular, for tire treads of racing tires, comprising at least one diene rubber, at least one filler, plasticizers, and further usual additives, characterized in that it has, relative to 100 parts by weight of the entire rubber components, 5 to 90 phr of at least one sheet silicate that is modified with alkylammonium ions of the general formula $^+NR_4$ and is free of additional guest molecules polymerized or swelled in by a prior treatment.
2. Rubber mixture according to claim 1, characterized in that it contains 40 to 85 phr of sheet silicate.
3. Rubber mixture according to at least one of claims 1 through 3, characterized in that the separate layers of the sheet silicate have a layer thickness of 0.8 to 2.0 nm and a mean diameter of 80 to 800 nm.
4. Rubber mixture according to at least one of claims 1 to 4, characterized in that the modified sheet silicate has a carbon content of 5 to 50 percent by weight.
5. Rubber mixture according to at least one of claims 1 through 5, characterized in that the R in the alkylammonium ion can be identical or different and are selected from the group consisting of hydrogen, substituted or unsubstituted, saturated or unsaturated alkyl groups with 1 to 40 carbon atoms with or without branches, and substituted or unsubstituted aryl and benzyl groups, with at least one R being a substituted or unsubstituted, saturated or unsaturated alkyl group with more than 8 carbon atoms.
6. Rubber mixture according to at least one of claims 1 through 6, characterized in that

the alkylammonium ion is a dimethyl dioctadecylammonium ion.

7. Rubber mixture according to at least one of claims 1 through 6, characterized in that the diene rubber or the diene rubbers is or are selected from the group consisting of natural rubber, synthetic polyisoprene, polybutadiene, and styrene-butadiene-copolymer.
8. Rubber mixture according to at least one of claims 1 through 8, characterized in that it comprises 2 to 50 phr of at least one plasticizer oil.
9. Rubber mixture according to at least one of claims 1 through 8, characterized in that it contains 0 to 85 phr, preferably 5 to 50 phr, carbon black as an additional filler, with the sum of the portions of carbon black and sheet silicate in the mixture not exceeding 90 phr.
10. Rubber mixture according to at least one of claims 1 through 9, characterized in that it contains at least one silane coupling agent.
11. Vehicle tire, in particular, racing tire, containing a tread that consists at least partially of a sulfur-cured rubber mixture according to at least one of claims 1 through 10.